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(54) Title: RUBBER COMPOSITION COMPRISING CARBON NANOTUBES AS REINFORCING AGENT AND PREPARATION THEREOF

(57) Abstract: The present invention provides a rubber composition in which synthetic rubber or natural rubber, including natural rubber (NR), styrene-butadiene rubber (SBR) and polybutadiene rubber (BR), is reinforced with carbon nanotubes or graphitic nanofibers, and a process for preparation thereof. According to the present invention , application of the physical and mechanical properties of carbon nanotubes or graphitic nanofibers to rubber can result in rubber products which have improved mechanical, physical and chemical properties, compared with existing rubber products reinforced with carbon black or silicone.

RUBBER COMPOSITION COMPRISING CARBON NANOTUBES AS REINFORCING AGENT AND PREPARATION THEREOF

Technical Field

The present invention relates to a rubber composition comprising carbon nanotubes or graphitic nanofibers (GNF) as a reinforcing agent, and a process for preparation thereof. More particularly, the present invention relates to a process for preparation of a rubber composition, characterized in that carbon nanotubes or GNF, or a mixture of carbon nanotubes or GNF with carbon black or silicone which are conventionally used as a reinforcing agent for rubber, are used as a reinforcement to improve the mechanical, physical, electrical or chemical properties of the rubber composition, and a rubber composition prepared by said process.

Technical Background

Traditionally, rubber products have been synthesized using carbon black or silicone (silane compounds) as a reinforcing agent to enhance the tensile stress or durability of the rubber. However, a carbon nanotube, which is an allotrope of carbon black in the aspect of basic structure, is superior to carbon black in strength and has a tensile stress as high as 100 times that of steel. It also has excellent properties such as high elasticity, high conductivity and the like.

A carbon nanotube consists of a carbon atom bound to three adjacent carbon atoms, the bonding between those carbon atoms resulting in a hexagonal cyclic structural unit. A number of such units form a plane of repeated hexagonal structures in the form of honeycomb, and the plane rolls into a cylindrical tube to finally constitute a nanotube.

Such a carbon nanotube has a diameter in the range of several angstroms to several nanometers, and the ratio of its length to diameter ranges from tens to thousands. Extensive researches on the synthesis of carbon nanotubes are being carried out because the nanotubes have a morphological feature as mentioned above and have good thermal, mechanical and electrical properties resulting from their

characteristic chemical bonding. It is expected that utilization of those properties would lead to the development of many new products that are technically limited in the selection of materials, and to the rendering of new properties to existing developed products. Especially, when carbon nanotubes form composites with polymers, tensile stress as well as the desired properties of the materials such as the electrical and chemical properties would be maximized. In particular, formation of composites is expected to contribute in improving tensile stress, elasticity, electrical properties, durability and the like, which are known to be weak points of polymers [Erik T. Thostenson, Zhifeng Ren, Tsu-Wei Chou, Composites Science and Technology 61(2001) 1899-1912].

For a polymer product using carbon nanotubes as a reinforcing agent, it was reported that when polystyrene was added with only 1 % by weight of carbon nanotubes, the tensile stress and elastic stiffness of the product increased by about 25 % and 36-42 %, respectively [Qian D, Dickey EC, Andrews R, Rantell T. Applied Physics Letters, 2000:76(20):2868-2870].

R. Andrews and Y. Chen et al. reported that single wall nanotubes could be used as reinforcement for petroleum pitch fiber. They demonstrated that when even 1 % by weight of carbon nanotubes was used as a reinforcing agent, tensile stress, elastic coefficient and electric conductivity increased greatly, and when 5 % by weight of single wall nanotubes were used, tensile stress, elastic coefficient and electric conductivity increased by 90 %, 150 % and 340 %, respectively. Particularly, they predicted that since the aromatic properties of petroleum pitch are similar to the aromatic properties of nanotubes, the bonding strength would be high [R. Andrews, et al., Applied Physics Letters, 75(1999) 1329-1331].

As such, when fabricating composite structures, addition of even a small amount of carbon nanotubes may maximize the properties of the polymers themselves. However, the results of these researches were obtained by using carbon nanotubes of very high purity, i.e. more than 99 % of purity, since when the purity of the carbon nanotubes used as reinforcement for polymer is low, the carbon black that is formed during the synthesis of carbon nanotubes results in the lowering of the strength.

Thus, although a small amount of carbon nanotubes is added as reinforcement, the composite materials become expensive owing to the carbon nanotubes of high purity. Further, in the case of polymers comprising saturated hydrocarbons, their affinity with carbon nanotubes decreases, thereby resulting in the limitation in obtaining desired strength.

However, since most of rubbers are unsaturated hydrocarbons, they show good affinity with carbon black or carbon nanotubes, and also may lead to the production of new composite rubbers having higher tensile stress, wear resistance and durability than the traditional rubbers comprising carbon black only, even though rubbers are synthesized with a mixture of low-purity carbon nanotubes and carbon black. Therefore, it is expected that products stronger than traditional products may be prepared using a relatively inexpensive mixture of low-purity carbon nanotubes and carbon black instead of costly high-purity carbon nanotubes. This is advantageous in that inexpensive, low-purity carbon nanotubes or GNF that are thermally synthesized in conventional carbon black preparation processes, without using various synthesis methods for carbon nanotubes that are known to produce high-purity carbon nanotubes, such as the arc discharge method, laser vaporization, chemical vapor deposition (CVD), catalytic synthesis, plasma synthesis and the like. This is also advantageous in that synthetic rubber materials that use carbon nanotubes as reinforcement can be obtained at relatively low production costs, compared with traditional rubber products.

The rubber composite materials thus synthesized using carbon nanotubes or GNF as reinforcement may be used in those traditional fields where existing rubber products are used as well as in a variety of new fields such as electromagnetic wave shielding materials. Especially, when synthetic rubbers such as natural rubber (NR), styrene butadiene rubber (SBR) and polybutadiene rubber (BR) are used with reinforcements like carbon nanotubes or GNF, the products are expected to have improved tensile stress, higher elasticity and higher wear resistance than traditional tires.

Summary of the Invention

The inventors of the present invention discovered that rubbers with higher tensile stress and improved properties such as electrical properties, wear resistance and elasticity, compared with traditional rubber products, can be synthesized by substituting all or a part of the carbon black or silicone, which are traditionally used as reinforcement to improve specific properties of rubbers, with carbon nanotubes or graphitic nanofibers (GNF), and attempted to develop a process for preparation of rubbers with improved distribution of carbon nanotubes or GNF in the rubber.

Accordingly, the present invention provides a rubber composition containing carbon nanotubes or graphitic nanofibers (GNF) as a reinforcing agent.

Detailed Description of the Invention

According to the present invention, the rubber composition may be a rubber composite or may have a composite structure.

According to the present invention, a rubber composition with higher tensile stress and improved properties such as electrical properties, wear resistance and elasticity, compared with traditional rubber products, is provided by replacing all or a part of carbon black or silicone reinforcement with carbon nanotubes or GNF.

In the present invention, the type of rubber is not particularly limited, and mention may be made on a rubber selected from the group consisting of natural rubber, synthetic rubbers based on diene polymers or copolymers (e.g., polybutadiene, styrene-butadiene rubber, polyisoprene rubber, etc.), nitrile rubbers, silicone rubbers, neoprene rubbers, butyl rubbers, Thiokol (polyalkylene sulfide), urethane rubbers (polyesters and polyethers), ethylene-propylene rubbers, epichlorohydrin rubbers, epichlorohydrin-ethylene oxide rubbers, chlorosulfonated polyethylene rubber (Hypalon), polyacrylate rubbers, fluorine rubbers, and mixtures thereof.

In the present invention, the type of carbon nanotubes or graphitic nanofibers is also not particularly limited, and all types of single wall carbon nanotubes, all types of multi-wall carbon nanotubes, all types of GNF, and mixtures thereof may be mentioned. The shapes of carbon nanotubes or GNF (for example, helical, linear,

branched types) are not particularly limited, as long as the nanotubes are necessary for improving specific properties of rubbers.

Moreover when carbon nanotubes or graphitic nanofibers are used as a reinforcing agent for rubbers, carbon nanotubes may be doped with H, B, N, O, F, Si, P, S or Cl, or may be reacted with at least one from transition metal atoms or transition metal compounds, or alkaline metal atoms, in order to improve specific properties or the affinity for rubber.

The carbon nanotubes or graphitic nanofibers that can be used for the present invention may be prepared by conventional preparation methods, and in particular by the process for preparation of carbon nanotubes or graphitic nanofibers described in Korean Patent Application No. 2001-43659 (Filing date: July 20, 2001) by the Applicant of the present invention.

According to a preferred embodiment of the present invention, the methods of improvement for more uniformly distributing carbon nanotubes or graphitic nanofibers in the rubber are also included in the scope of the present invention. Uniform distribution of additives such as carbon nanotubes in the rubber allows the expression of improved properties that are characteristic to the carbon nanotubes in composite structures such as rubber compositions.

For example, addition of surfactants allows more uniform distribution of carbon nanotubes or GNF in the rubber. Gong, et al. reported that using nonionic surfactants in an epoxy resin reinforced with carbon nanotubes helped to improve uniform distribution of nanotubes in polymers and to strengthen the bonding between polymers and nanotubes [X. gong, et al., Chemistry of Materials 12(2000), 1049-1052].

Such role of surfactants is also advantageous in uniformly distributing carbon nanotubes or GNF in rubber. The surfactants used for this purpose may be cationic, anionic or nonionic, and are not limited in type as long as they distribute carbon nanotubes or GNF uniformly in the rubber and improve the properties by strengthening the bonding. Therefore, according to the present invention, surfactants as well as stearic acid or fatty acids may be added.

In the present invention, carbon nanotubes or graphitic nanofibers are used in an amount of 0.1 to 150 %, preferably 0.2 to 120 %, and more preferably 0.5 to 100 % by weight of the rubber.

These carbon nanotubes or graphitic nanofibers may be used in a mixture or compound with carbon black or silicone products that are traditionally used as reinforcements. In this case, the amount of carbon nanotubes or graphitic nanofibers may range, with respect to the content of carbon black or silicone product or a mixture of the two, from 0.1 to 99.9 %, preferably from 0.1 to 99 %, and more preferably from 0.5 to 90 % by weight, and if necessary, an amount not more than 50 % by weight can also be used.

In the present invention, synthetic rubbers that are prepared by reinforcing synthetic rubbers for automobile tires, such as natural rubber (NR), butadiene rubber (BR), styrene-butadiene rubber (SBR), with carbon nanotubes, may be an advantageous material for tires. Therefore, according to a modification of the present invention, provided are automobile tires and a process for preparation thereof using a rubber composition containing carbon nanotubes or graphitic nanofibers as reinforcement.

Generally, the largest portion in the consumption of rubber is used in the synthesis of rubber for tires. In this regard, when carbon nanotubes are used as reinforcement for rubber, it is found to be possible to produce tires much stronger than conventional tires, with expected increases in tensile stress or elasticity, and improved wear resistance. Further, since carbon nanotubes show good elastic strength or electric conductivity and can achieve desired properties with addition in even smaller amounts, they can be used in more various applications than the conventional rubber products reinforced with carbon black.

Examples

The present invention will be explained in detail with reference to the following examples, which are not intended to limit the present invention.

Example 1

Natural rubber was used as the raw material for rubber, and additives that are generally used in the synthesis of rubber for tires were used.

The amounts of the additives used in testing the properties of synthetic rubber reinforced with carbon nanotubes were as follows: on the basis of the content of natural rubber, 5 % by weight of carbon nanotubes used as a reinforcing agent (multi-wall carbon nandtubes of an average diameter of 60 nm), 45 % by weight of carbon black, 2 % by weight of elemental sulfur, 4 % by weight of zinc oxide and 0.4 % by weight of an accelerator. The composition was basically similar to the compositions generally used in the synthesis of rubber for tires. Vulcanization was carried out at 150°C for 30 minutes.

The tensile stress of thus obtained synthetic rubber was 32.1 MPa, and the stress at 300 % strain was 29.7 MPa. These values, obtained in the case of using a mixturc of carbon nanotubes and carbon black, represent increases by about 35 % for tensile stress and about 37 % for the stress at 300 % strain, compared with the case of using carbon black only.

Comparative Example 1

Natural rubber (NR) was used as the raw material for rubber, and additives that are generally used in the synthesis of rubber for tires were used.

The composition was the same as that used in Example 1, except that carbon nanotubes were not used, and included, on the basis of the amount of natural rubber (NR), 50 % by weight of carbon black reinforcement (N-330 having a particle size of 32 nm), 2 % by weight of elemental sulfur, 4 % by weight of zinc oxide and 0.4 % by weight of an accelerator. Vulcanization was carried out at 150°C for 30 minutes.

The tensile stress of thus obtained synthetic rubber was 23.8 MPa, and the stress at 300 % strain was 21.7 MPa.

Example 2

The amounts of the additives used in testing the properties of synthetic rubber reinforced with carbon nanotubes were as follows: on the basis of the amount of rubber (NR), 5 % by weight of carbon nanotube reinforcement (multi-wall carbon nanotubes with an average diameter of 60 nm), 25 % by weight of silicone, 2 % by weight of elemental sulfur, 4 % by weight of zinc oxide and 0.4 % by weight of an accelerator. The composition was the same as that used in Comparative Example 2 below, except that 5 % by weight of carbon black was replaced with carbon nanotubes. Vulcanization was carried out at 150°C for 30 minutes.

The tensile stress of thus obtained synthetic rubber was 23.8 MPa, and the stress at 300 % strain was 21.7 MPa. These values, obtained in the case of using a mixture of carbon nanotubes and silicone, represent increases by about 32 % for tensile stress and about 41 % for the stress at 300 % strain, compared with the case of using silicone only.

Comparative Example 2

In this experiment, changes in the properties of rubber composition were observed when a portion of carbon nanotube reinforcement was replaced with silicone reinforcement.

Natural rubber (NR) was used as the raw material for rubber, and additives that are generally used in the synthesis of rubber for tires were used. The composition was basically similar to the compositions generally used in the synthesis of rubber for tires, and included, on the basis of the amount of rubber (NR), 30 % by weight of silicone reinforcement having a particle size of 32 nm, 2 % by weight of elemental sulfur, 4 % by weight of zinc oxide and 0.4 % by weight of an accelerator. Vulcanization was carried out at 150°C for 30 minutes.

The tensile stress of thus obtained synthetic rubber was 2 MPa, and the stress at 300 % strain was 19.5 MPa.

From the above Examples, it is found that tensile strength can be remarkably improved with replacement of carbon black or silicone with only a small amount of

carbon nanotubes for the reinforcement of rubber.

Industrial Applicability

According to the present invention, synthesis of composite rubbers by substituting all or a part of carbon black or silicone which is used as reinforcement for rubber, with carbon nanotubes or GNF can result in materials with higher tensile strength and elasticity than conventional products, and which materials are highly resistant to structure deformation or destruction.

In particular, when applied to automobile tires, products having better mechanical properties than those reinforced with carbon black or silicone can be obtained.

WHAT IS CLAIMED IS:

1. A rubber composition containing carbon nanotubes or graphitic nanofibers (GNF) as reinforcement.

2. A rubber composition according to Claim 1, characterized in that the rubber is selected from the group consisting of natural rubber, synthetic rubbers based on diene polymers or copolymers (e.g., polybutadiene, styrene-butadiene rubber, polyisoprene rubber, etc.), nitrile rubbers, silicone rubbers, neoprene rubbers, butyl rubbers, Thiokol (polyalkylene sulfide), urethane rubbers (polyesters and polyethers), ethylene-propylene rubbers, epichlorohydrin rubbers, epichlorohydrin-ethylene oxide rubbers, chlorosulfonated polyethylene rubber (Hypalon), polyacrylate rubbers, fluorine rubbers, and mixtures thereof.

3. A rubber composition according to Claim 1, characterized in that the carbon nanotubes or graphitic nanofibers (GNF) are single wall carbon nanotubes, multi-wall carbon nanotubes, graphitic nano-fiber (GNF), or mixtures thereof.

4. A rubber composition according to Claim 3, characterized in that the carbon nanotubes or graphitic nano-fibers are those representing straight, helical or branched shapes, or mixed shapes, or a mixture of those with different shapes.

5. A rubber composition according to Claim 3 or 4, characterized in that the carbon nanotubes or graphitic nanofibers (GNF) are doped with H, B, N, O, F, Si, P, S, or Cl, or contain at least one from transition metals, transition metal compounds or alkaline metals.

6. A rubber composition according to Claim 1, characterized in that said composition is in the form of composites using surfactants, stearic acid or fatty acids.

7. A rubber composition according to Claim 6, characterized in that the surfactants are cationic, anionic, nonionic or mixtures thereof.

8. A rubber composition according to Claim 1, characterized in that the carbon nanotubes or graphitic nanofibers are contained in an amount of 0.1 – 150 % by weight on the basis of the amount of rubber.

9. A rubber composition according to Claim 1, characterized in that the carbon nanotubes or graphitic nanofibers are used as a mixture or a compound with carbon black or silicone products.

10. A rubber composition according to Claim 9, characterized in that the carbon nanotubes or carbon nanofibers are contained in an amount of 0.1 – 99.9 % by weight on the basis of the amount of carbon black or silicone product, or of a mixture thereof.

11. Automobile tires using a rubber composition according to Claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR03/00078

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08K 7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC7 C08K 7/06, 7/24
IPC7 C01B 31/00, 31/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Patents and applications for inventions since 1975
Korean Utility models and applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
FPD, PAJ, USPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	US 6426134 B (E.I.du Pont de Nemours and Company) 30 July 2002 (30.07.2002) See the whole document	1,3
A	EP 1054036 A (FINA RESEARCH S.A.) 22 November 2000 (22.11.2000) See the whole document	1
P,A	JP 2002-97375 A (TORAY IND INC) 2 April 2002 (02.04.2002) See the whole document	1
P,A	JP 2002-338220 A (OSAKA GAS CO.LTD.) 27 November 2002 (27.11.2002) See the whole document	5
A	JP 1996-325195 A (NEC CORP) 10 December 1996 (10.12.1996) See the whole document	5

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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EP 1054036 A	22.11.2000	NONE	
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